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XI. *Experiments and Observations relating to the Principle of Acidity, the Composition of Water, and Phlogiston.* By Joseph Priestley, LL.D. F. R. S.

Read February 7, 1788.

THAT water consists of two kinds of air, dephlogisticated and inflammable, is now, I believe, generally admitted as one of the most important, and best ascertained, doctrines in chemistry. My own experiments having seemed to favour it, I made no difficulty of receiving it myself: but having, at the time of the publication of the last Volume of my Experiments, found that, in decomposing the two kinds of air above mentioned by the electric spark, I got much less water than I expected, and, instead of it, a dark-coloured vapour, not easily condensed, I could not help concluding that something yet remained to be investigated with respect to this subject, and determined, at a proper opportunity, to resume my inquiries into it.

At that time, however, I had no suspicion of any *acid* being produced in the process; having never been able to find any in the water which I had hitherto procured in pretty large quantities from the decomposition of those two kinds of air, though the doctrine of dephlogisticated air being, or containing, the principle of *universal acidity*, had been advanced by M. LAVOISIER, and admitted by myself and others.

Suspecting that much of the water which had been procured

in the above-mentioned process was no proper constituent part of the air, but only such as had been diffused through it, and in some manner attached to it, and kept suspended in it, and therefore might be separated from it, without decomposing the air; on resuming these experiments, I used every precaution I could think of to detach all water from the air on which I operated. In order to this, I kept it confined by mercury, together with a quantity of *fixed ammoniac*, which imbibes water more readily, if not in greater quantity, than quick-lime, or any other known substance.

In this more accurate method of making the experiment, I was gradually led to discover the acid, which had escaped my observation before. But I am not certain that I should have found it even now, if I had not been aided by the sagacity of Mr. KEIR, who was always of opinion, that some acid *must* be the produce of this experiment, or rather that the produce would be something which would become acid by exposure to the open air.

I began with making the explosions in the same glass vessel from which the mixture of air had displaced the mercury with which it had been filled; when I found, as I have observed in my last publication, the whole of the vessel was filled with a dense smoke, which settled into a black coating of all the inside of the vessel, and which appeared, as before, to be mercury; becoming white by exposure to the air. For some time I perceived no appearance of *water*: but placing the vessel at a proper distance from a fire, I found about a quarter of a grain collected on the opposite side; when, as the vessel contained four ounce measures of air, the water produced ought to have been at least a grain.

The

The mercury being an impediment in this process, I afterwards confined the mixture of air in one vessel (with mercury and fixed ammoniac as before) but I made the explosions in another, which I had previously exhausted of air. This vessel was larger than that which I had used before, containing something more than eight ounce measures; so that the air it contained, being one-third dephlogisticated and two-thirds inflammable, would have weighed about two grains. After one explosion the quantity of water collected appearing inconsiderable, I repeated the process in the same vessel, and then collecting the water, I found it not to exceed a grain and an half.

I repeated this experiment very often, and constantly found some water, but it always fell far short of the weight of the air decomposed. There must, therefore, have been something not very fluid adhering to the sides of the vessel, which could not be dislodged by a moderate heat; and indeed the glass did not recover the perfect clearness that it had before the process.

I always observed, that, presently after every explosion, the vessel was filled with a dense vapour, so that it was sometimes impossible to see through it; and before I admitted the external air, I could pour it from one end of the vessel to the other, and it seemed to fall almost as fast as a feather in a common vacuum, and in general it did not disappear in less than ten minutes. I even found this dense vapour when the mixture of air had been confined by water. The smell of the vessel, after the process, was that of the most offensive kind of inflammable air from iron.

From these experiments it was sufficiently evident, that something more than *water* had been produced; and pouring into the vessel a quantity of the juice of litmus, it was instantly turned to a deep red; so that it was equally evident, that

that an *acid* had been formed. In all the preceding experiments the dephlogisticated air had been procured from manganese; and in all the experiments mentioned in this Paper, the inflammable air was from iron by water only.

A great number of strong glass vessels having been broken in these experiments, and sometimes with some hazard to myself, and the quantity of air that I was able to decompose in them being small, I next procured a *copper* vessel, which contained about thirty-six ounce measures of air; and having now no other object than discovering the *kind* of acid that I had procured, I made repeated experiments in it; and after every ten or twelve explosions collected all the liquid matter I could find; which, as the air had been previously confined by water, was pretty considerable, about equal to the weight of the air.

The liquor that I procured in this manner was always of a deep blue or green, being evidently a solution of copper. But it also contained a redundant acid, as appeared by its turning the juice of litmus red. Besides this blue liquor, there was always a quantity of seemingly abraded copper; for it was perfectly and quickly dissolved by volatile alkali, as copper very minutely divided would have been.

In these experiments I used, at different times, dephlogisticated air from manganese, from red precipitate, and from red lead, as the most unexceptionable of all; and as it was obligingly furnished me by Mr. KEIR, the preparation of it may be depended upon. There did not, however, appear to be any other difference in the liquors produced by means of these kinds of dephlogisticated air, except in the shade of the colour; that from manganese being of the deepest blue, and that from red lead the lightest; and this difference might be accidental.

By

By the assistance of Mr. KEIR I examined these solutions of copper, and presently found, by means of a solution of terra ponderosa in spirit of salt, that it was not, in any of the cases, the vitriolic; and yet, as the dry substance left by the evaporation of the liquor did not deliquesce, I had concluded, that the acid was neither the nitrous, nor the marine; but Mr. KEIR informs me, that this is the case with a fully saturated solution of copper in spirit of nitre.

Also Dr. WITHERING, who was so obliging as to examine some of these liquors for me (for, not being much accustomed to these analyses, I had requested him to undertake it) had procured from that in the production of which the *red lead* had been used, crystals of nitre, and other indisputable indications of nitrous acid; so that I was satisfied that it was this acid that was produced in all the cases.

I had a farther proof of the acid being the nitrous, that having (in order to get a quantity of liquor that should be as little saturated with any metal as possible) used a vessel of *tinned iron*, I found, that after some time, when the tin had been much corroded (and with every process a considerable quantity came away) the liquor, which at first was colourless, was tinged with red. In these experiments I made use of dephlogisticated air from red lead.

As both the kinds of air made use of in these experiments were exceedingly pure, it seems evident, that phlogisticated air does not contain all the elements of nitrous acid; but only supplies a *base* for it, the dephlogisticated air (which was used in a greater proportion in the valuable experiment of Mr. CAVENDISH) supplying the acidifying principle, as I had conjectured in the last Volume of my Experiments, p. 404. Besides, though all phlogisticated air could not be excluded in those

experiments in which the air-pump was used, this objection cannot well be made to those in which that instrument was not used; and in them the slowly condensable vapour above mentioned seems to be an evident symptom that the produce was not mere water. But it is a satisfactory answer to this objection, from the presence of *phlogisticated air* in the tube, that this kind of air is not decomposed, or at all affected, by this process, as will be found by mixing any quantity of it with the two other kinds of air.

That a considerable quantity of water enters into the composition of dephlogisticated air, will not be thought improbable, when it is considered that, in my former experiments, this appeared to be the case with respect to *inflammable air*. For without water this air cannot be procured. I can also now say, that the same is the case with respect to *fixed air*. It is not therefore improbable, that the same may be true of every other kind of air, since water is used in the production of them all.

Terra ponderosa aerata (a substance of which Dr. WITHERING has given us an excellent analysis) gives no fixed air by mere heat. But I find, that when steam is sent over it, in a red heat, in an earthen tube, fixed air is produced with the greatest rapidity, and in the same quantity as when it is dissolved in spirit of salt: and, making the experiment with the greatest care, I find, that fixed air consists of about half its weight of water.

From two ounces of the terra ponderosa I got, by means of steam, 190 ounce measures of fixed air, so pure that at first 150 ounce measures of it were reduced by agitation in water to  $3\frac{1}{2}$ , and of the last produce, 30 ounce measures were reduced to one. Examining the residuum of the first portion by means of nitrous air, I found it to be of the standard of 1.5.

After

After this, attending to the water expended in the process, I found that I procured 330 ounce measures of fixed air with the loss of 160 grains of water. According to this, as the air weighed 294 grains, the water in the fixed air must have been 80 parts of 147 of the whole.

In another experiment, having previously found that three ounces of the terra ponderosa yielded about 250 ounce measures of fixed air, I attended only to the loss of water in procuring it, and I found it to be about one-fifth of an ounce, in two successive trials. The quantity of fixed air would weigh 225 grains, and the water expended about 100 grains; so that, in this experiment also, the fixed air must have contained about one-half of its weight of water.

That water enters into the composition of fixed air, and adds considerably to its weight, is farther probable from the solution of terra ponderosa in spirit of salt. Because when the solution is evaporated to dryness, and the residuum exposed to a red heat, the weight of the air, and of this residuum, exceeds that of the substance from which it was procured; and it is probable, that a red heat would expel any marine acid adhering to it.

Forty-eight grains of terra ponderosa dissolved in spirit of salt, and then evaporated to dryness, and exposed to a red heat, lost four grains, and yielded eight ounce measures of fixed air, which would weigh 7.2 grains; consequently, three-sevenths of the weight of the air was something that had been gained in the process, and therefore probably water.

The near coincidence of the results of these different experiments is remarkable, and makes it almost certain, that no marine acid is retained in the terra ponderosa that has been dissolved in it, after exposure to a red heat; that the generation

of the fixed air carries off part of the water in the menstruum; and that this part of the weight is about one-half of the whole.

I must observe, that the supposition of water entering into the constitution of all the kinds of air, and being, as it were, their proper *basis*, that without which no aëriform substance can subsist (which the preceding experiments render in a high degree probable) makes it unnecessary to suppose, as myself as well as others have done, that water consists of dephlogisticated air and inflammable air, or that it has ever been either composed or decomposed in any of our processes.

That water is decomposed when inflammable air is procured from iron by steam, is not probable; since the inflammable principle may very well be supposed to come from the iron, and the addition of weight acquired by the iron may be ascribed to the water which has displaced it. Also when the *scale of iron, or finery cinder,* is heated in inflammable air, it gives out what it had gained, *viz.* the water.

The most plausible objection to this hypothesis is, that iron gains the same addition of weight, and becomes the same thing, whether it be heated in contact with steam, or surrounded by dephlogisticated air. But from the preceding experiments it appears, that by far the greatest part of the weight of dephlogisticated air is water; and the small quantity of acid that is in it may well be supposed to be employed in forming the *fixed air*, which is always found in this process: for that there is one common principle of acidity, and that all the acids are convertible into one another (at least the nitrous acid into fixed air) is by no means an improbable supposition, though we are not yet in possession of any process by which it may be done. It is pretty evident that, in this respect, nature actually does what we are not able to do.

In my last Volume of Experiments, I recited the particulars of one, the result of which seemed to be dissimilar to this with the scales of iron and inflammable air; for heating *red precipitate* in inflammable air, I then found little or no water; but having used more precautions, I have since found it in sufficient quantity in this process, even though the inflammable air was previously well dried with fixed ammoniac. In this experiment I discontinued the process after three ounce measures of air were absorbed, leaving room in the vessel, that the moisture might be more easily collected. With this precaution, and warming the vessel, I collected between an half and three-fourths of a grain of water.

This experiment may be thought to be unfavourable to my present hypothesis, as all water was carefully excluded, and yet a sufficient quantity was found in the process. But besides taking into the account the water that is necessary to constitute the inflammable air, why may not *red precipitate*, in its dryest state, be supposed to contain water, as well as the scales of iron, which will bear any degree of heat without parting with it. Red precipitate is made by a liquid process, and therefore the water, that may enter into its composition as a calx, may quit it when it becomes a metal.

I shall take the liberty to observe farther, that the doctrine of the *decomposition of water* being set aside, that of *phlogiston* (which, in consequence of the late experiments on water, has been almost universally abandoned) will much better stand its ground, as all the newly discovered facts are more easily explained by the help of it.

If water be not decomposed, both metals and sulphur do certainly yield inflammable air, when steam is made to pass over them in a red heat. They cannot, therefore, be *simple substances*,

stances, as the antiphlogistic theory makes them to be. Also, the same thing that they have parted with, *viz.* inflammable air (or rather something that is left of inflammable air when the water is taken from it, and which may as well be called phlogiston as any thing else) may be transferred to other substances, and thus contribute to form any of the metals, sulphur, phosphorus, or any thing else that has been deemed to contain phlogiston. This phlogiston also, no doubt, having weight, it perfectly corresponds to the definition of a *substance*, having certain affinities, by means of which it is transferred from one body to another, as much as the different acids.

If there be no such thing as one principle of phlogiston, transferable from one substance to another, it must be admitted, that inflammable air from sulphur is real sulphur and water, that from iron, iron and water, as well as that very different substance, the *scale of iron*. And since copper, or any other metal, may be made of inflammable air from iron, &c. all the metals will be, in fact, convertible into one another. At least, it may be said, that all the component parts of any one metal may be so incorporated with any other, that no test can detect it. Also iron, made of inflammable air from sulphur, ought, upon this hypothesis, to have the properties of *sulphurated iron*, which undoubtedly it would not have. An hypothesis loaded with these difficulties must be inadmissible; whereas that of phlogiston is extremely simple, and, as far as appears, of universal application.

The discovery that the greatest part of the weight of inflammable air, as well as of other kinds of air, is water, does not make the use of the term phlogiston less proper: for it may be still given to that *principle*, or thing, which, when added to water, makes it to be inflammable air; as the term

oxygenous principle may be given to that thing which, when it is incorporated with water, makes dephlogisticated air.

As there is something in dephlogisticated air that seems to be the principle of *universal acidity*, so I am still inclined to think, as I observed in my last Volume of Experiments, that phlogiston is the principle of *alkalinity*, if such a term may be used; especially as alkaline air may be converted into inflammable air.

In the course of experiments recited in this Paper, I discovered more completely than before the source of my former mistake, in supposing that fixed air was a necessary part of the produce of red lead, and also of manganese. Both these substances, I find, give of themselves only dephlogisticated air, and that of the purest kind; and all the fixed air they yielded in my former experiments must have come from the gun-barrel I then made use of, which would yield inflammable air, which, with dephlogisticated air, forms fixed air. For though the dephlogisticated air from red lead was so pure that, mixed with two measures of nitrous air, the three measures were reduced to five hundredth parts of a measure, and the substance gave no fixed air at all when it was heated in an earthen tube or retort; yet by mixing iron filings with it, or with manganese, as I had formerly done with red precipitate, I got more or less fixed air at pleasure, and sometimes no dephlogisticated air at all.

